Critical Raw Materials Hungary Data Collection 2. Minor element enrichments in certain sedimentary mineral formations

A Kritikus Nyersanyagok Magyarország Adatgyűjteményből 2. Ritkaelem-dúsulások értékelése egyes üledékes nyersanyag előfordulásainkban

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A team of Hungarian and international students from the TEKH College of the Faculty of Earth and Environmental Science Engineering (University of Msikolc) in their 2024 work program started the remapping of Hungarian critical element occurrences, first of all with regard to our coal basins and the sedimentary rocks in western Mecsek. The analysis obtained on historic data are often unreliable, but they are still sufficiently accurate to highlight and compare different critical element enrichments. Looking at the examples in our recent study from an economic point of view, the elements showing the most promising enrichment are Sc, Be, Hf, Ge and V, but RFFs, Ta, Nb, Ga and PGEs are also enriched.

Among the sites presented in the article, Máza (Sc, LRFF, Hf, Nb, Ta, PGE), Komló (Be, Sc, V, HREE), Pécs-Szabolcs (Be, Ga, Ge, Nb, HREE), Bükkábrány (Sc) and Bánhorváti (Ge) deserve special attention. It is increasingly important to get reliable information about the geology, resource, availability of critical raw materials within borders. The approach which has been offered in our article may be a contribution in this regard. The database behind the discussed enrichments, occurrences can be accessed through the TEKH website [3].

Keywords: critical raw materials, Hungary, coal, uranium ore, copper ore, sedimentary deposits

A Miskolci Egyetem TEKH Kollégiuma a 2024. évi munkaterve alapján megkezdte a hazai kritikus elemi előfordulások feltérképezését, elsőként a szénmedencéink és a nyugat-mecseki üledékes kőzetek esetében. A rendelkezésre álló adatokon alapuló értékelések sok hibával terheltek, de így is elegendőek a különböző kritikus elemdúsulások kiemeléséhez és összehasonlításához. Közgazdasági szempontból vizsgálva a legutóbbi tanulmányunkban szereplő példákat, a vizsgált földtani környezetekben a legígéretesebb dúsítást mutató elemek az Sc, Be, Hf, Ge és V, de a ritkaföldfémek, Ta, Nb, Ga is mutatnak gazdaságossághoz közeli koncentráció értékeket.

A cikkben bemutatott lelőhelyek közül Máza (Sc, LRFF, Hf, Nb, Ta, PGE), Komló (Be, Sc, V, HREE), Pécs-Szabolcs (Be, Ga, Ge, Nb, HREE), Bükkábrány (Sc) és Bánhorváti (Ge) külön figyelmet érdemel. A kritikus ásványi nyersanyagok kutatásában egyre fontosabb a megbízható információk megszerzése a geológiáról, az erőforrásokról, a kritikus nyersanyagok határainkon belüli elérhetőségéről. A cikkünkben felkínált megközelítés hozzásegíthet ehhez. A tárgyalt dúsítások, előfordulások mögötti adatlapok a TEKH honlapján [3] érhetők el.

Kulcsszavak: kritikus nyersanyagok, Magyarország, szén, uránérc, rézérc, üledékes nyersanyagok

1. Introduction

The College of Natural Resources Research and Utilization (TEKH) of the Technical Faculty of Earth and Environmental Sciences of the University of Miskolc is renovating information on the EU's critical and strategic raw materials as part of a self-developed project [1]. Regarding the summarization of general information related to critical and strategic elements in the first article the global review on the battery raw materials has now been completed and it has been published [2].

A systematic database of more detailed geological, chemical, and technological data is being built, hopefully for the benefit of as many interested readers, researchers, and professionals as possible [3].

2. The sources of information

The outcomes of the previous CriticEl program have been served as basis [4]. At the time, the listed 14 critical raw materials has since been expanded to 34 items. We also used basic data collected, systematized and not yet published in this program during 2012– 2014. Publicly accessible items of the state geological archive was also searched. In addition publicized site-specific geochemical data were searched and evaluated. In the case of the raw materials included in the list for the first time, the retrospective literature search was extended to the 1950s.

We took into account the occurrences for which geochemical or mineralogical information based on analyzes was available. The approximate extraction benchmark is considered if the current total local value estimated from the average concentration of strategic and critical raw materials reaches or exceeds USD 10 per tons of the raw material [1]. This does not represent an economic opportunity, but it effectively separates the background type of data from the enrichment opportunities that deserve attention.

We used the USD as a value indicator because many raw materials are quoted and traded in this currency on the world market. It should be noted that prices can fluctuate significantly even within a short period of time. This article records the situation in January 2024. The content of our data sheets available on the Internet will be actualized regularly.

The geographical location of the occurrences included in the summary is summarized on the map in *Figure 1*.



Figure 1. Location map of the mentioned critical element occurrences (see Table 3)

3. Strategic and critical element anomalies in Hungarian coal deposits

During the period of the Green Transition, special emphasis is placed on the opportunities that open up alternative applications of coal rocks that are no longer used for energy production. Research into the extraction of other materials that can be produced as by-products from coal began in Hungary in the 1950s. Most of the data come from the 1960–1970 period, the peak period of Hungarian coal mining, although their quality is unfortunately poor by today's standards.

Within the framework of CriticEl and in the subsequent period, a small number of, but reflecting the development of exploration and analysis technologies, much higher quality geochemical data was produced. In the case of all three domestic types of coal (black coal, lignite, lignite), there are new data, some of which deserve further investigation.

3.1. Hard coals and related sedimentary rocks – Eastern Mecsek

The Lower Jurassic hard coal occurrences of Eastern Mecsek have the most significant minor element anomalies and the largest number of new analysis results. The geochemical sampling of the formations of the coal basin and its surroundings began in the 1950s, and research has been continued in many stages and institutes to this day. The most important previous research information was created between 1971 and 1985 [5-7]. Based on these, the anomalously enriched minor elements of the area were rare earths (REE), Ge, Be, Nb, Ta, Zr and Hf. The most important known enrichment centers are Pécs-Vasas and Pécs-Bányatelep (Karolina valley). The results of the Máza-Váralja area during coal explorations in the 1980s are encouraging (Table 1) (based on 100 assayed samples, these are maximums from all of the assayed samples). Subsequent sampling and analyzes during the CriticEl program and later projects confirmed the enrichment [8–10], with the exception of germanium, which is still being investigated.

 Table1. Maximum values recorded during the Máza-Váralja coal explorations. Source: [6]

Element	g/t	Element	g/t
Zr	10000	La	500
Мо	150	Yb	100
Sc	200	Hf	100
Y	1000	Та	20

Total REE maximums in the historic assays exceed 1800 g/t value. In the modern assays the average TREE values oscillate from 140 to 1400 g/t. Averages oscillate between 140 and 530 ppm.

Outlier maximums are located mainly on the northern occurrences (Komló, Máza, Nagymányok).

Here the enrichment of REE compared to the hard coal average contents is significant (with an enrichment factor of 5-10), and also the degree of enrichment of Ge and Be in the historic records, which re-

quires further control (and can be economically very significant if proven).

In most cases, we find some type of intruding later Mesozoic alkaline magmatites nearby (in some places along the contact zone causing development of natural coke from the coal), which may be the magmatic source of the rare element enrichments in the rocks of the coal series.

The enrichments occur partly in coal seams and partly in the accompanying sedimentary rocks of the clay, carbonaceous clay or claystones, with peaks of chemical composition that are different for each occurrence, but mostly strongly exceed the trace element content of the coals. In all cases, Nb and Zr, as well as Ta and Hf associated with them, show a significant enrichment (exceeding 10 times the world average typical for hard coal).

The REE enrichments are closely correlated with the distribution of thorium, which was previously recorded by aerial radiometric measurements for the entire Mecsek area. The territorial distribution of the maxima on the Th map shows a good agreement with the territorial distribution of the Mecseki Kőszén Formation. This realization can be the basis of a research methodology to be further developed in the future.

3.2. Brown coals and related sedimentary rocks

We have few and sporadic chemical analyzes of our brown coal basins. There are no evaluable data from the formations of the basins around Sopron, Hidas, Tatabánya and Dorog.

a) Ajka

Early geochemical sampling and analysis campaigns revealed that the coal has an anomalously enriched V and U content. In the geochemical summary of the Ajka II area, the vanadium content of the ash as an average of 263 samples was 593 mg/kg, with a peak value of 1600 g/t [11]. In a later series of 12 samples, the average value of vanadium in the ash was 600 mg/kg, with a peak value of 6830 g/t [12].

b) Észak-Bakony

MTA GKL tested 12 samples from 3 deep drillings for 11 trace elements in 1990 using AAS technology [13]. The RFF elements were not included among the analyzed components. Anomalous nickel content (max. 2000 g/t) and vanadium (max. 900 g/t) appeared among the values for critical elements.

c) Nógrád és Borsod

Regarding the strategic and critical raw material sources, the investigations of the last century were

aimed at assessing the Ge content of the brown coals of the Borsodi and Nógrád basins [14]. The analyzes were partly made with traditional chemical analytical methods and partly with spectral analysis. The highest outlier Ge values occurred in three areas in Borsod: Bánhorváti (301 g/t), Sajókaza (182 g/t) and Kondo (168 g/t). In the Bánfalva 39 drillhole the average value for Ge obtained in the 239-248 m section of drilling is 175 g/t, which can reach the commercial threshold. In Nógrád, in some of Kazár's drillings, the average Ge content exceeded the reference value (K-420 18 g/t Ge).

Recently, PTE examined coal and shale samples taken from the Kazár and Felsőnyárád open pits using the AAS method for Ga, Ge, Be elements [15], with maximum values of 35 and 26 g/t Ge.

3.3. Low-grade lignites and related sedimentary rocks

Of our known low-grade lignite areas (Várpalota, Torony, Bódva völgy, Mátra- and Bükkalja), of Miocene to Pliocene periods only the last two occurrences were known to have a systematic geochemical tests that covered both seams and waste rocks. These also only cover a small proportion of the elements classified as critical and strategic today, and their analysis accuracy is outdated by today's standards.

During the lignite explorations in Mátra and Bükkalja in the 1960–1970s, geochemical analyzes were also carried out on some of the drilling samples. These studies provided data on the distribution of Be, Ni, Cu, B, Ga, In, Ge, As, and V among the critical elements. Among those listed, the anomalous enrichment amounts of Be, B and V reported in some sampled core sections are currently still being processed in GIS.

In unpublished analyzes after sampling related to the 2018 national coal project, Sc (60 g/t in the coal ash) appeared in anomalous concentrations in the Bükkábrány mine.

4. Paleozoic and Mesozoic formations of Western Mecsek

Western Mecsek has given rise to intensive geological exploration programs in several stages (uranium ores, radioactive waste disposal site tests). Despite this, there is very little useful data on critical and strategic elements.

4.1. Boda Claystone Formation and Korpád Sandstone Formation

The oldest known enrichments were formed at the border of the BAF and the variegated sandstone assemblage. Its anomalous Cu concentrations should be highlighted (0.08–1%). Knowledge is primarily limited to open-pit excavations, but the Ibafa-4 drilling also defined an enriched section with Cu and Ag anomalies [16].

4.2. Kővágószőlősi Sandstone Formation (U-bearing sandstone).

We have not yet found detailed published summary data on the geochemistry of Mecsek uranium ore. The early investigations recognized significant V content (max. 1000 g/t) in the Cr-containing hydromicas accompanying uranium mineralization should be high-lighted [17].

In the 1991 MÉV examination of 25 hand samples, 6 samples from the deposit contained Cu (>0.2%), 1 sample As (1%), 5 samples Sc (>100 g/t), 11 samples Ti (>1%), 9 samples were anomalous in terms of V (>200 g/t), 5 samples Mn (>1%), 1 sample Nb (>400 g/t). It is likely that a large number of internal company reports may still contain data, which the processing team has not yet reached.

4.3. Patacsi Siltstone Formation

The Cu (-Ag) enrichments occurring in the Permian – Lower Triassic transitional series in the overlying Permian productive uranium ore formations deserve special attention. The anomalies have been known for decades [18, 19] in Pécs-Égervölgy. Analyzes related to these were also included in the 1991 MÉV tests, the approximate average quality of the few samples analyzed here is about 0.5 % Cu + 30 g/t Ag. In a broader sense, their stratigraphic position and lithological characteristics are similar to the Silesian black shale major ore deposit (Kupferschiefer) in southern Germany and Poland. Mineralogical studies of this analogy has already been completed [20]. Based on

mineralogical tests, cobalt minerals can also be identified in samples enriched in Cu-Ag components.

An enrichment center that has not been interpreted geologically, but with well-known mineralogical information, is the copper mineralization in the vicinity of Kozári Vadászház, Pécs.

5. Access to further detailed information

The information of each occurrence is summarized in a respective data-sheet, and downloadable from the TEKH College website [3]. For sake of convenience, each occurrence is numbered using the postal code. Same postal codes indicate the geographical position of the occurrences in the map of Hungary. Same postal codes mark the occurrences on the location map.

6. Integral evaluation, ranking of exploration potential

The collected data are far from sufficient to reliably estimate the economic potential of occurrences. The reason for this is the small number of data, their heterogeneity in terms of time, space and sampling and analysis method, and the fact that the mineral resources and processing technology are not known. But what is certain is that enrichments represent opportunities to varying degree. We definitely wanted to convey this expressively, i.e. we tried to rank the known enrichments, partly according to types of materials and partly according to places of occurrence.

In the evaluation, we limited ourselves to critical and strategic types of primary sources of raw material. The enrichments may contain other significant value generators (e.g. gold, silver, zinc, lead, etc.), but we did not include them. We did not take into account

Table 2. The Hungarian occurrences and the related anomalies

Postal code	Site	Critical raw material	Postal code	Site	Critical raw material
3127	Kazár	Ge	7300	Komló	Nb, Ta, LREE, HREE, Hf, Be
3422	Bükkábrány	Sc	7351	Máza	Nb, Ta, LREE, HREE, Hf, Be
3535	Miskolc-Diós- győr	Ge	7355	Nagymányok	Nb, Ta, LREE, HREE, Hf, Be
3642	Bánhorváti	Ge	7628	Pécs-Kozár	Cu
3704	Berente	Ge	7634	Pécs-Égervölgy	Cu, Co
3720	Sajókaza	Ge	7673	Kővágószőlős	V, Cu
3721	Felsőnyárád	Ge	7691	Pécs-Vasas	Nb, Ta, LREE, HREE, Hf, Be
3732	Kurityán	Ge	7694	Hosszúhetény	Nb, Ta, LREE, HREE, Hf, Be
3770	Sajószentpéter	Ge	7720	Pécsvárad	Nb, Ta, LREE, HREE, Hf, Be
3775	Kondó	Ge	7935	Ibafa	Cu
3778	Varbó	Ge	8056	Bakonycsernye	V, Ni
3779	Alacska	Ge	8400	Ajka	V

the possible advantages and disadvantages of interference, i.e. the problem regards to several raw materials appearing together.

From the 34 raw materials in the current CRM list, we omitted those which are not directly related to mineral raw materials (phosphorus, metallurgical coke, natural graphite). We further reduced the remaining 31 types of materials by those that do not have an accepted global market, and/or we did not find an acceptable market price as a benchmark (bauxite, feldspar, helium) in public information.

The types of raw materials listed in groups were then broken down into the chemical elements: Light Rare Earth Elements (LREE), Heavy Rare Earth Elements (HREE), Platinum Group elements (PGE), and the values obtained for the individual elements were summed up in the line of the group name. The way of the grouping of elements is on geochemical basis, also found on the SCRREEN website [21].

6.1. Experimental ranking by occurrence and by raw material

We created a table showing value indicators broken down by occurrences and types of raw materials (Table 2). In it, the columns are given by the critical element grade indicators at individual occurrences, and the rows by the individual types of raw material.

6.2. Grade indicators

We included in the evaluation all occurrences for which geochemical information is available and at least one of the critical/strategic element components exceeded the 10 USD/tons threshold value (Table 2). In these cases we calculated with the concentrations of every strategic elements.

It should also be noted that the samples linked to the data used are in most cases the "by-products" of research or exploration conducted on occurrences for other purposes, and are not representative samples of the enrichment of the elements sought.

The number of samples producing the available data on individual occurrences also differed by orders of magnitude, at this stage we simply calculated arithmetic averages without any adjustment to the different amount of samples, or consideration to outliers which may distort the mean values.

In the case of several unmergeable data sets of an occurrence, we used the most recent (and therefore presumably the most accurate) analyses in this summary.

6.3. Price indicators

We worked with global market prices that were available on the Internet at the time of the investigation. They are very diverse, and set on different bases. Where possible, we used 1) spot prices of pure metals in USD, 2) prices quoted as annual average prices in either the SCRREEN or in the Mineral Commodity Summary (USGS) databases. The current price indicator list and their sources can be found on our website [3].

6.4. Value indicators

In the following, we chose the solution of giving the anomalous element an estimated value as the product of the two factors based i.e. the grade indicator and the price indicator. In the same occurrence (for example 7300 Komló: 1191), several types of critical material may be anomalously enriched, these have been aggregated according to the occurrence. Enrichments formed in several occurrences of one type of material (for example, value indicator of Beryllium: 1021) were summarized at the end of the horizontal rows of the material types. The new information generated in this way has no real economic meaning, but it can identify the types of raw materials that promise the most positive results, and the areas of occurrence that promise the most important opportunities.

The score is zero if 1) no analyzes were made, or 2) analyzes were made, but based on their concentration value, the local value of the elements does not reach the minimum lower value limit of USD 10/tons. In other cases, the scores are the product of the average concentration and the unit price shown in the left column of the table.

In the very first row above the critical elements, the score obtained as the sum of the values of all known critical elements for the given occurrence is listed. The column following the last occurrence shows the score characteristic of each type of material, which is obtained as the sum of the scores in the columns of the listed occurrences.

The top summary row (Occurrence-VI) summarizes the value indicators for each occurrence, and provides approximate information on the ranking between the evaluated occurrences. The last summary column (CRM VI) summarizes the value indicators by raw materials, and provides ranking between raw material types (for the occurrences in evaluation).

The outlined solution contains a number of arbitrary approximations and simplifications, and in no way indicates any economic judgement. However, it offers a preliminary, easy-to-use processing and comparison tool for a large number of inhomogeneous geochemical data, and at the same time it also provides an opportunity to give ranking to geographical entities, i.e. facilitates geospatial visualization.

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	/692	Pécsbányatelep	218	0	0	0	51	0	0	0	0	0	0	14	69	0	0	0	0	2	0	3	11	0	0	0	0	65	1	0	0	0	0
1001	/ 691	Pécs-Vasas	167	0	0	0	11	0	0	0	0	0	0	0	0	0	0	15	0	17	0	0	18	0	0	0	0	71	0	0	0	35	0
V C J C	/b34	Pécs-Égervölgy	42	0	0	0	0	0	0	0	42	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	735	λογnἑmy _{3e} N	79	0	0	0	10	0	0	0	0	0	0	1	0	0	4	5	0	6	0	2	0	1	0	0	0	35	1	0	0	7	0
urrences	/351	szèM	1342	0	0	0	0	0	0	0	0	0	0	0	0	0	457	1	0	22	0	0	87	0	0	29	0	745	0	1	0	0	0
critical element occurrences	/ 300	komló	1191	0	0	0	937	0	0	1	1	0	0	17	36	0	0	13	2	11	0	2	18	3	0	0	0	66	15	0	0	38	0
melen melen	3/80	ξdelény	15	0	0	0	0	0	0	0	0	0	0	0	15	0	 0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
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Kankin 2770	3//0	Sajószentpéter	19	0	0	0	0	0	0	0	0	0	0	0	19	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
table 3. Kanking table	3/32	Kurityán	52	0	0	0	0	0	0	0	0	0	0	0	52	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1	3/21	Felsőnyárád	11	0	0	0	0	0	0	0	0	0	0	0	11	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
FOFC	3/04	Berente	12	0	0	0	0	0	0	0	0	0	0	0	12	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
.,,,	3642	itåvnodnåß	210	0	0	0	0	0	0	0	0	0	0	0	210	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1010	3535	Miskolc-Diósgyőr	21	0	0	0	0	0	0	0	0	0	0	0	21	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	3422	Bükkábrány	223	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	223	0	0	0	0	0
10.10	312/	Kazár	94	0	0	0	4	0	0	0	0	0	0	0	22	0	0	0	0	0	0	0	0	0	0	0	0	50	0	0	0	19	0
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	Ket.date	2024-01-17	Occurrence	As	в	barit	Be	Bi	barit	Co	Cu	fluorit	földpát	Ga	Ge	grafit	Hf	HREE	Li	LREE	Mg	Mn	Nb	Ni	foszfát	PGE	Sb	Sc	Sr	Та	Ti	>	×

Table 3. Ranking table of critical element occurrences

6.5. Interpretation of the ranking table

From *Table 3*, among the critical and strategic material types, the following main conclusions can be drawn:

- Among the critical raw materials, based on the current data, the five metals with the greatest economic potential in the studied deposit groups: Sc, Be, Hf, Ge, V, and the rare earth metals (LREE, HREE) have a smaller weight.
- Among the occurrences, the first five are the most important: Máza (Sc, LREE, Hf, Nb, Ta, PGE), Komló (Be, Sc, V, HREE), Pécs-Bányatelep (Be, Ga, Ge, Nb, HREE), Bükkábrány (Sc), Bánhorváti (Ge).

It should be stressed again, that the value indicators are formed using prices of metals, irrespective of their production, etc. costs and market demand evaluation, thus they do not reflect economic value of the occurrence.

Similar simple perspectivity tables can be compiled if enrichment factors (element contents divided by clarke values) are formed for each element and each occurrence.

7. Summary

As part of the Critical Elements Marathon, the TEKH College of the University of Miskolc has started the mapping of Hungarian critical element occurrences, first of all with regard to our coal basins and the sedimentary rocks in western Mecsek. The analysis obtained on available data are often very approximate, but they may serve to highlight and compare different critical element enrichments.

Looking at the examples in our recent study from an economic perspective:

- the elements showing the most promising enrichment are Sc, Be, Hf, Ge and V, but REE's, Ta, Nb, Ga and PGEs are also enriched.
- Among the sites presented in the article, Máza (Sc, LREE, Hf, Nb, Ta, PGE), Komló (Be, Sc, V, HREE), Pécs-Szabolcs (Be, Ga, Ge, Nb, HREE), Bükkábrány (Sc) and Bánhorváti (Ge) deserve special attention.

It is increasingly important to evaluate the available information about the geology, resource, availability of critical raw materials within our borders. Our approach may be a small but simple contribution in this regard.

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